Wall-Induced Orientational Order of a Liquid Crystal in the Isotropic Phase—an Evanescent-Wave-Ellipsometry Study

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Using an evanescent-wave ellipsometric technique, we have studied the wall-induced orientational order in the isotropic phase of 4′-*n*-pentyl-4-cyanobiphenyl (5CB) at a silane-treated glass surface. Near the isotropic-nematic transition temperature T_{NI}, a *weak* nematic layer appears at the interface with its thickness exhibiting a critical divergence as $T \rightarrow T_{NI}$ according to $(T - T_{NI})^{-0.5}$. This observed pretransitional behavior is qualitatively at variance with the existing theories.

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A properly treated solid surface can preferentially orient liquid crystal (LC) molecules in their mesophases.[1] The effect is the result of anisotropic interactions between the molecules and the solid surface and is essential for the construction of many LC devices. These molecule-substrate interactions could induce an orientational order of the LC molecules near the solid surface even when the bulk LC is in the isotropic phase. Such a wall-induced pretransitional behavior has been studied theoretically, first with the Landau–de Gennes formalism[2–4] and, more recently, in terms of wetting phenomena[5–7] with the wall-induced nematic order viewed as "wetting" of the isotropic LC-solid interface by a nematic layer.

Despite its theoretical and practical interest, experimental studies of the wall-induced orientational ordering have been scarce. So far, the only quantitative work reported in the literature was by Miyano[8] and Tarczon and Miyano[8] and van Sprang;[9,10] both have used transmission ellipsometric techniques. The overall induced birefringence of the interface layer was measured as a function of temperature. Their results were analyzed and interpreted in terms of the Landau–de Gennes theory. There are obvious limitations in this approach: (1) The probe beam passes through both the interfacial and the bulk regions; any spurious birefringence induced in the bulk would be difficult to eliminate. (2) Since only the overall birefringence is measured, the local induced birefringence at the wall and the characteristic thickness of the interfacial layer cannot be deduced separately.

Aiming at eliminating these limitations so that more critical comparison with theories could be made, we have developed an improved ellipsometric technique using an evanescent probe beam in a total-reflection geometry. Consider a laser beam incident upon a LC-substrate interface from the substrate side. Total reflection occurs when the angle of incidence is above a critical angle, and the optical field on the LC side becomes evanescent. Since an evanescent optical wave is bounded at the interface, it is particularly sensitive to optical properties of the interfacial region. Furthermore, its penetration depth can be adjusted by variation of the incident angle. Thus, information about the interfacial layer at various depths can be deduced from a scan of the incident angle. This then allows a separate determination of the wall-induced order parameter and the interfacial layer thickness. *In situ* monitoring of the bulk LC is also made possible through a measurement of the critical angle, which depends only on the refractive index of the bulk LC relative to that of the substrate. In this respect, bulk and interfacial contributions to the properties of the reflected beam are easily distinguishable. This is particularly important for studying interfacial phenomena near a bulk transition, and, in addition, makes the study of the nematic LC-solid interface possible.

Using the evanescent-wave ellipsometry technique, we have studied the wall-induced orientational order in the isotropic phase of 4′-*n*-pentyl-4-cyanobiphenyl (5CB) at a glass surface coated with N,N-dimethyl-N-octadecyl-3-aminopropyl-trimethoxysilyl chloride (DMOAP). Our technique had a sensitivity better than the transmission ellipsometric techniques by a factor of 5 or more. The induced order parameter at the wall and the interfacial layer thickness (coherence length ξ) could be determined for each temperature T independently. For $T \gtrsim T_{NI}$ (isotropic-nematic transition temperature), we found a weak wall-induced nematic layer at the interface; its order parameter at the wall was nearly independent of temperature, but the coherence length ξ diverged according to $(T - T_{NI})^{-0.5}$ as $T \rightarrow T_{NI}$. Although the observed exponent (0.5) of the coherence length agrees with the value given by the Landau–de Gennes theory, the observed "complete wetting" behavior (i.e., $\xi \rightarrow \infty$ as $T \rightarrow T_{NI}$) with a relatively small induced order parameter is not predicted by it, nor by the wetting theories.[5,6]

In our experiment, the liquid crystal 5CB was obtained from BDH, Inc., and used without further purification. Its isotropic-nematic transition occurred at 35.0°C, with a coexistence width of ~100 mK. As shown in Fig. 1, the sample assembly consisted of a glass prism (Schott glass LaSF 5), a glass plate, and a 130-μm layer of 5CB sandwiched between the prism and the

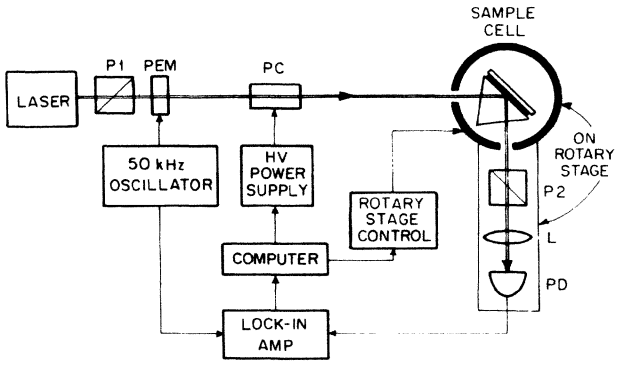

FIG. 1. Experimental arrangement. P1, polarizer; P2, analyzer; PEM, photoelastic modulator; PC, Pockels cell; L, lens; PD, photodiode.

plate. Both glass surfaces sandwiching the LC were coated with a monolayer of silane surfactant molecules, DMOAP, to assure homeotropic alignment for 5CB in the nematic phase.[11] The sample assembly was situated in a two-stage oven with its temperature stabilized to ~ 1 mK. The experimental arrangement is depicted in Fig. 1. A weak He-Ne laser beam at $\lambda = 6328$ Å was used as the probe light. The phase difference $\Delta\phi$ between the p- and s-polarization components of the reflected beam was measured with basically the standard high-resolution ellipsometry technique.[12] We were able to achieve an accuracy of 1×10^{-4} rad in the measurements of $\Delta\phi$.

The sample cell was mounted on a rotary stage driven by a stepping motor. The beam angle of incidence θ could then be varied by a rotation of the sample cell. Angular scans of phase retardation, $\Delta\phi(\theta)$, were made for a series of temperatures at $T > T_{NI}$, decreasing from high to low. Before a run at a certain T, ample time ($\sim\frac{1}{2}$ h) was allowed for the LC to reach thermal equilibrium. The results are shown in Fig. 2(a). The glass prism contributed a small but nonnegligible background in $\Delta\phi(\theta)$ due to its residual stress birefringence. Through measurement of the $\Delta\phi(\theta)$ of the sample cell with the LC replaced by an isotropic liquid (Dow-Corning 702 silicone fluid was used), the background $\Delta\phi(\theta)$ ($\sim$0.01 rad) was determined. Over the temperature range under study, this background was roughly independent of temperature. The bulk phase transition and the isotropic-nematic coexistence region were easily recognizable through a significant change in the shape of the $\Delta\phi(\theta)$ curve and the position of θ_c. At a given temperature $T > T_{NI}$, $\Delta\phi(\theta_c)$ [see Fig. 2(b)] is a visual indication of the interfacial ordering effect. This quantity would vanish in the absence of an interfacial layer.

Figure 2(a) shows a monotonic increment of θ_c with decreasing T. This is due to the temperature dependence of the bulk optical dielectric constant ε_l for the isotropic phase. The curves also exhibit clearly a $\Delta\phi(\theta_c)$ that

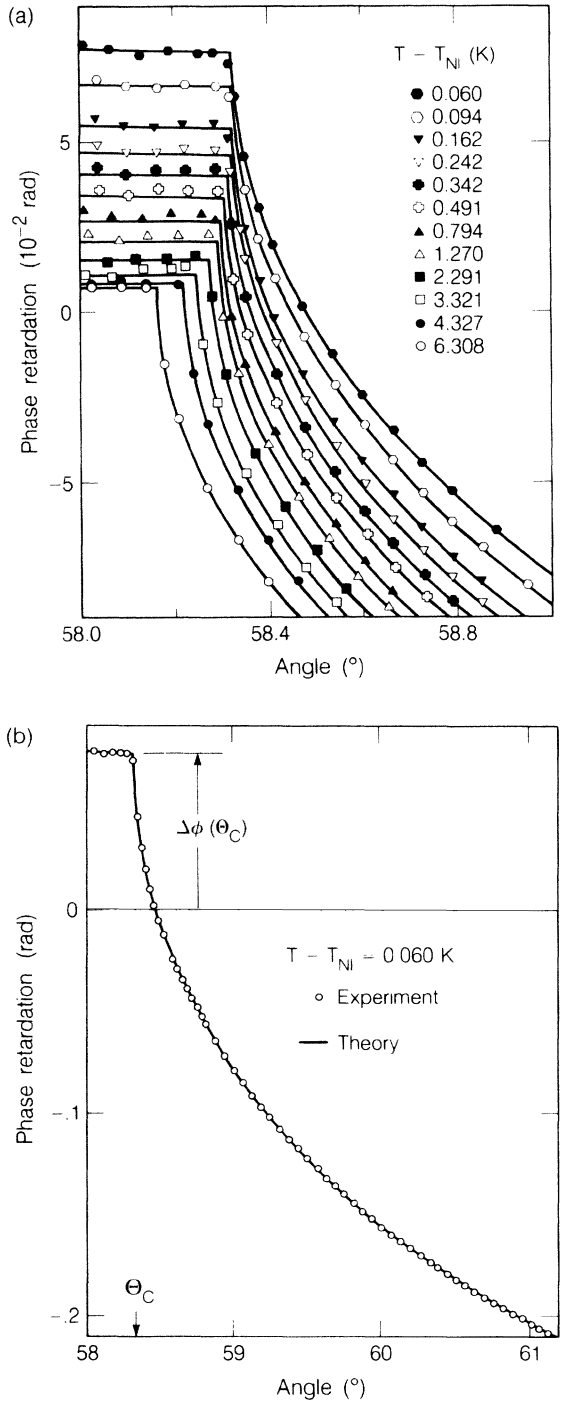

FIG. 2. (a) $\Delta\phi(\theta)$ curves at $T > T_{NI}$. Only the portion around θ_c is displayed. Solid curves were obtained from theoretical calculations. (b) A typical $\Delta\phi(\theta)$ curve with the background subtracted (see text).

diverges as T approaches T_{NI}. The existence of a wall-induced ordering effect with a strong pretransitional behavior is thus apparent even in the raw data. The divergence of $\Delta\phi(\theta_c)$ as $T \rightarrow T_{NI}$ is a result of the diver-

gence of the coherence length ξ, as we shall discuss below.

To fit the data of $\Delta\phi(\theta)$ at a given T, we assumed an anisotropy in the optical dielectric constant as

$$\Delta\varepsilon(z)=\varepsilon_{\parallel}(z)-\varepsilon_{\perp}(z)$$
$$=\Delta\varepsilon_0\exp(-z/\xi) \quad \text{for } z\geq 0, \tag{1}$$

where $z=0$ refers to the boundary surface between the LC and the glass prism, and both $\Delta\varepsilon_0$ and ξ could be functions of temperature. This assumption can be justified from the Landau-de Gennes theory if $\Delta\varepsilon_0$ is sufficiently small,[4] which is true in our case. We used the 4×4 matrix technique developed by Berreman and Scheffer[13] to calculate the linear wave propagation in the LC medium and consequently $\Delta\phi(\theta)$, treating $\Delta\varepsilon_0$ and ξ as adjustable parameters, and then a nonlinear least-squares fit procedure to deduce $\Delta\varepsilon_0$ and ξ. The theoretical curves in Fig. 2(a) thus obtained are in excellent agreement with the experimental ones, with an average error estimated to be 1×10^{-4} rad. An example showing the detailed fit is presented in Fig. 2(b). The critical angle for total reflection θ_c is determined solely by the bulk optical constants ε_l for the LC and ε_g for the glass through the relation $\theta_c=\sin^{-1}(\varepsilon_l/\varepsilon_g)^{1/2}$, as long as the penetration depth ($>\lambda/2\pi\sqrt{\varepsilon_l}$) of the optical wave is larger than the thickness (<400 Å in our case) of the interfacial layer.

We found that $\Delta\varepsilon_0=0.081\pm0.018$, which is essentially a constant in the temperature range studied. This corresponds to a temperature-independent boundary order parameter $Q_0\equiv\Delta\varepsilon_0/\Delta\varepsilon_m\simeq0.077\pm0.017$, where $\Delta\varepsilon_m$ is the maximum value of $\Delta\varepsilon$ when all molecules are perfectly aligned.[14] We notice that Q_0 is much smaller than the bulk order parameter $Q\geq Q_c(T=T_{NI})\simeq0.33$ in the nematic phase.[15] The accuracy of $\Delta\varepsilon_0$ was limited by the resolution of $\Delta\phi$ in our measurements. The values of ξ deduced for various T can be described by the function

$$\xi(T)=6.6(T/T_c-1)^{-0.51}\ \text{Å}, \tag{2}$$

with a standard deviation of 2.8 Å (Fig. 3). The optimum fit was obtained with $T_c=T_{NI}-40$ mK, which falls within the isotropic-nematic coexistence region ($T_{NI}\pm50$ mK).

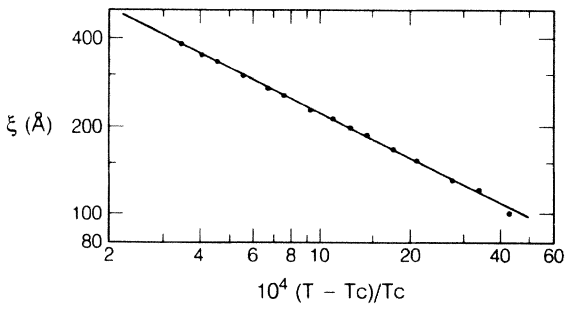

FIG. 3. Coherence length of the interfacial layer as a function of the reduced temperature (on log-log scales). The solid line is described by Eq. (2).

According to the Landau-de Gennes theory, in the limit of sufficiently weak boundary order, the coherence length should have the form $\xi=\xi_c=\xi_0(T/T'-1)^{-1/2}$, where T^* describes the bulk supercooling limit.[4] For 5CB, $T^*=T_{NI}-1.1$ K,[16] $\xi_0\simeq5$–6 Å.[9,17] In Eq. (2), both the exponent ($\simeq\frac{1}{2}$) and the length scale (6.6 Å) agree closely with those of ξ_c, but the critical temperature T_c appears to be near T_{NI}, instead of T^*.[18] Physically, we do not expect the critical behaviors of the interfacial coherence length ξ and the bulk correlation length ξ_c to be the same. We note that ξ_c is the average size of the nematic domains in the isotropic background, and these domains are uncorrelated. At the interface, however, an in-plane, long-range orientational correlation is established by the wall-anchoring force. Such an in-plane correlation is likely to enhance the correlation along the surface normal, and lead to a critical behavior of ξ different from that of ξ_c.

Our observation that ξ diverges at $T_c\simeq T_{NI}$ corresponds to the complete wetting of the isotropic LC-solid interface as $T\rightarrow T_{NI}$. This is not predicted by the existing theories. Both the Landau-de Gennes theory[2-4] and the wetting theories[5,6] have indicated that complete wetting may occur when $Q_0\gtrsim Q_c$ (bulk nematic order) as a result of a divergent growth of a plateau in the profile of $Q(z)$. We found, however, complete wetting with a relatively weak wall-induced nematic ordering ($Q_0\ll Q_c$) without incurring any prewetting transition, at variance with theoretical prediction.

Another descrepancy between theory and experiment is in the temperature dependence of Q_0. The theories predict that Q_0 becomes weakly dependent on temperature only when the wall-anchoring force is very strong, leading to a large value of Q_0 ($>Q_c$). Experimentally, we found an approximately temperature-independent Q_0 with $Q_0\ll Q_c$. Recently, Guyot-Sionnest, Hsiung, and Shen[19] have also observed a dipole layer of 8CB at an 8CB-DMOAP-coated-glass interface, which does not change its character over a wide range of temperature.

Finally, we compare our results with those obtained by Miyano[8] from a similar 5CB-DMOAP-coated-glass interface. Using the Landau-de Gennes theory, he deduced a value $Q_0=0.169$ (with $\xi_0=6$ Å) for the interfacial layer, which only partially wetted the isotropic LC-solid interface at $T=T_{NI}$ (i.e., ξ remained finite at T_{NI}), in contrast to our observation. Aside from the limitations in Miyano's measurement discussed earlier, we may attribute the differences to his use of a continuous temperature scan in the measurements and a background level as an adjustable parameter in fitting the data.

Modifications of the existing theories are clearly needed to explain our observation. Further experimental

studies would also help to obtain a more complete picture of the wetting behavior. The wall potential can be varied systematically by different surface treatment. Liquid crystals in a homologous series bounded to the same substrate can be studied. Our technique could also allow the investigation of the LC-solid interface with the bulk LC in the nematic phase and will provide important information on how the surface ordering Q_0 varies across T_{NI}. One interesting possibility is the observation of "drying" of a solid surface by an interfacial layer with $Q_0 < Q$ (bulk). The results of the recent experiment by Faetti *et al.*[20] indicated that this could be the case for 5CB on a glass substrate coated with obliquely evaporated SiO.

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